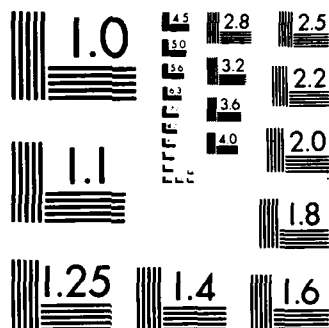


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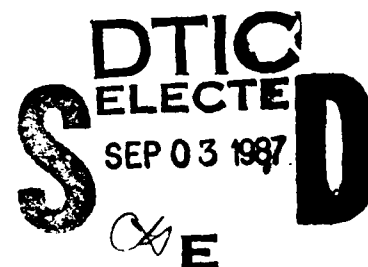
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FRANK J. SEILER RESEARCH LABORATORY

**CALCULATION OF THE TRIBOLOGICAL
PROPERTIES OF SURFACES BY
SEMI-EMPIRICAL METHODS**



Jon T. Swanson and James J. P. Stewart

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July 87



**AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE**

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This document was prepared by the Energetic Materials Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit number 2303-F3-05. Capt Jon T. Swanson was the project scientist.


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This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


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Calculation of the Tribological Properties of Surfaces by Semi-Empirical Methods

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USAF Academy, CO 80840

ABSTRACT

Several avenues were explored for obtaining a semi-empirical quantum chemical model of solid lubricants. In the case of diamond and graphite, clusters of approximately 40 atoms have been used to model the surface. Such clusters still may not be sufficient to model such phenomena as adsorption of small molecules on graphite.

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I. INTRODUCTION

→ One method of increasing the performance of aircraft engines is to operate the engines at higher temperatures. A critical technology in this application is lubrication at high temperatures. A thorough understanding of solid lubrication of ceramic materials is therefore required. This report details our initial attempts at preparing a semi-empirical quantum chemical model of solid lubricants.

In our initial study we focused on two areas of the problem. The first area was to determine the best approach to treating a model surface or lubricant. The selection was governed by providing a reasonable model without requiring an unreasonable amount of computer time for each calculation.

The second area concerned obtaining an estimate of the ability of the above models to calculate the relatively weak interactions which occur between surfaces and lubricants, and between the lubricants themselves. Our first concern was to reproduce the trends, rather than obtain the absolute values in these interactions.

II. MODELS OF SURFACES

There are two basic approaches to modeling a surface. Either one can attempt to model an infinite surface, such as a sheet of graphite, relying on an ordered repetition of units along the surface, or one can model a portion of the surface, using a big enough piece that edge effects are not important at the center. We have explored the feasibility of both approaches.

A. FULL SURFACE CALCULATIONS

Two approaches were considered for the calculation of a full surface, the tight binding model and the cluster model. In the tight binding model a series of Fock matrixes are constructed involving the interaction of the central unit cell with itself and each successive unit cell. These matrixes are used to calculate energies and charge distributions. In the cluster model, the unit cell is taken to be sufficiently large that interactions over a distance larger than the unit cell can be neglected. Thus a single Fock matrix can be constructed and

solved.

Using the MNDO solid state program MOSOL, heats of formation and interatomic distances of various solids were calculated. Results are summarized in Table 1.

Solid	Heat of Formation		Bond Length (Angs)	
	Calc'd	Expt'l	Calc'd	Expt'l
Graphite	5.2	0.0	1.432	1.421
Diamond	12.4	0.4	1.573	1.545
Silicon	-0.7	0.0	2.255	2.352
Cubic Boron Nitride	-33.8	-60.0	1.595	1.565

Table 1. Results of MOSOL calculations on solids.

The agreement with experiment is generally good. The results are of comparable accuracy with those from conventional MNDO calculations on molecules. The calculations are, however, extremely time consuming. For example, diamond, with two atoms per unit cell, requires approximately 24 hours of CPU time on a VAX 11/780. For systems of tribological interest, involving a tens of atoms or more, the method is prohibitively slow. A similar problem results with the full cluster calculations. We were thus forced to examine alternative methods of calculating solid surfaces.

B. PARTIAL SURFACE CALCULATIONS

Rather than work with an infinite surface, one can cap a cluster with hydrogens or with "dangling bonds", thus reducing the calculation to essentially a large molecule. By using a molecule to simulate a solid the time consuming operations of sampling the Brillouin Zone can be avoided. The question then becomes how large a molecule is needed to mimic a complete surface and how small a molecule can one get away with so as not to consume an inordinate amount of computer time. Since no studies have been done on cluster size using AM1, this the first point investigated.

Two compounds were chosen for study, diamond and graphite. These two materials provide a potential surface and a potential lubricant for the study. The materials also provide two different types of problems to investigate. Diamond is a rigid lattice, thus the cluster must have sufficient depth, as well as breadth to account for this rigidity. Graphite is a sheet, but also has a delocalized pi system, thus long range interactions will be important.

1. Modeling of Diamond Surfaces

The approach used for determining the required cluster size

for diamond involved calculating a diamond cluster with a C-H bond at the center of the top surface, with a single C-F bond, and a free valence. Thus the bond strength of the central bond could be calculated and a comparison of two interacting surfaces with either hydrogen or fluorine on the surface could be made. The bond strengths are particularly important, as the radical will try to assume a planar sp_2 configuration, which will be inhibited by the rigidity of the diamond surface.

Diamond was modeled with clusters using up to 41 carbon atoms in the cluster. The results are shown in figure 2.

Single Sheet	Delta H_{fH}	r_{C-H}	Delta H_{fHF}	r_{C-F}
CH_3	38.73	1.1120	-77.72	1.3143
C_4H_{10}	17.59	1.1295	-63.43	1.3315
C_7H_{22}	14.95	1.1278	-59.60	1.3251
$C_{13}H_{20}$	27.78	1.1259	-59.37	1.3258
$C_{22}H_{34}$	27.99	1.1253	-59.43	1.3267
$C_{31}H_{46}$	33.64	1.1255	-58.09	1.3322
Bulk Material				
$C_{13}H_{20}$	27.78	1.1129	-59.37	1.3258
$C_{14}H_{26}$	36.72	1.1209	-58.50	1.3282
$C_{26}H_{38}$	36.48	1.1250	-58.09	1.3301
$C_{26}H_{32}$	35.90	1.1241	-58.06	1.3315
$C_{35}H_{42}$	34.52	1.1280	-55.87	1.3365
$C_{41}H_{44}$	37.56	1.1225	-58.42	1.3354
$C_{44}H_{44}$		1.1232	-57.82	1.3380

Table 2. Results for Calculations of Diamond.

These results indicate that a cluster of at least 40 carbon atoms are required before the center of the diamond cluster no longer is affected by additional carbons added at the edges. It is interesting to note that the C-H bond strength converges to about 35 kcal, whether a flat extended sheet or a multi-layered sheet is used for the calculation. Either appears able to provide sufficient rigidity if enough atoms are employed in the cluster.

Several of these surfaces were placed together to calculate an interaction potential for the surfaces. The surfaces were constrained to lie along a line connecting the central C-H of C-F bonds. The results are shown in table 3.

C-H Surface	Force Attraction (kcal/mol)	H-H Separation (Angstroms)
CH ₃	0.24	2.243
C ₄ H ₁₀	0.21	2.275
C ₇ H ₂₂	1.05	2.601
C ₁₃ H ₂₀	1.34	2.229
C ₁₇ H ₂₆	1.74	2.316

Table 3. Interaction Potentials for Diamond.

When the central hydrogen is replaced by fluorine the surface becomes repulsive. The model thus appears to be reproducing at least the gross features of a diamond and fluorinated diamond. The calculations also need to be done with a completely fluorinated surface.

2. Modeling of Graphite Surfaces

Two approaches were taken to determining the ability of carbon clusters to model a graphite surface. First the geometries and ionization potentials of various size clusters were calculated and compared with experimental values. The results are shown in Table 4.

Cluster	Avg. C-C Bond Length (central ring)	Ratio Longest to Shortest Bond (central ring)	Ionization Potential
C ₆ H ₆	1.4064	1.0013	9.39 eV
C ₁₄ H ₁₀	1.4257	1.0226	8.05
C ₁₈ H ₁₂	1.4479	1.0327	8.51
C ₂₄ H ₁₈	1.4499	1.0028	8.08
C ₄₂ H ₁₈	1.4305	1.0034	7.84
C ₄₈ H ₁₈	1.4288	1.0204	7.66
C ₅₄ H ₁₈	1.4272	1.0032	7.46
tight binding	1.432		
experimental	1.421	1.0000	5.00

Table 4. Geometries and Ionization Potentials of Graphite Clusters.

Ideally a graphite surface should have all C-C bond lengths equal. From the table one can see that the equality of the bond lengths is primarily a function of the symmetry of the cluster. Only the D6h clusters have equal bond lengths and they are constrained as such by symmetry. In all cases the differences only amount to a few percent of the total bond length. The magnitude of the bond lengths have become quite close to experiment with the C₄₈ and C₅₄ clusters.

The ionization potentials are not expected to be in agreement with experiment, as these are a property of the entire extended pi system. The results show a gradual progression of the ionization potential toward the experimental value, but a full surface calculation would be required to reproduce experiment.

The real question in regard to graphite surfaces is whether interactions between graphite surfaces or graphite and other surfaces can be modeled. To examine this question we have begun looking at a number of small molecules adsorbed on our graphite clusters. The experimental values we are attempting to reproduce are shown in Table 5.

Molecule	Heat of Adsorption Kcal/mol
Hydrogen	1.293
Nitrogen	2.3
Methane	3.032
Ethane	3.8
Ethylene	4.4
Dimethyl ether	5.5
Propane	6.3
Chloroform	8.0
Carbon Tet	8.4
Benzene	9.3

Table 5. Heats of Formation of Small Molecules on Graphite.

The experimental values provide a nice trend in heats of adsorption. If we cannot duplicate the absolute values, which may very well be the case, we hope to duplicate the trend in heats of adsorption. Two clusters are being used in the study, C₂₄H₁₂ and C₅₄H₁₈, to examine the effect of cluster size on the results.

Initial results for hydrogen are not encouraging. Hydrogen was started at a number of initial geometries from one to three angstroms from the surface of the cluster. In each case the hydrogen was repelled from the surface. Hydrogen is, however, the most weakly adsorbed species in our study. Calculations are underway on several of the larger adsorbates on the graphite surfaces.

3. Dangling Bonds

The clusters calculated to date have used hydrogens to satisfy the valences at the edge of the cluster. Ideally, one would like to use atoms to satisfy these valences as close to a

bulk atom in the cluster as possible. One thus needs a bulk atom which itself has no valences that need to be satisfied. To provide this feature, a new bond terminating atom called a "capped bond" has been developed. The properties of the "capped bond" are as follows:

- a) No interactions past 1.7 angstroms.
- b) No charge transfer from neighboring atoms.

The Cb atoms are monovalent, subtending exactly one bond.

We have had trouble achieving SCF in capped bond diamond, and so have no results as yet. The capped bonds are not as useful for graphite, as they do not include p orbitals.

4. Computation Times

Computational times for a number of cluster calculations are listed in Table 6.

Graphite		Diamond plane	
C ₆ H ₆	0.15	C ₁₃ H ₂₀	1.46
C ₁₈ H ₁₂	4.02	C ₂₂ H ₃₄	15.99
C ₂₄ H ₁₂	12.50	C ₃₁ H ₃₄	34.18
		solid	
C ₄₂ H ₁₈	33.71	C ₁₇ H ₂₆	2.89
C ₅₄ H ₁₈	23.05	C ₂₆ H ₃₂	41.46
		C ₄₁ H ₄₄	87.14

Table 6. Time for Calculations on a VAX 11/780 (hours).

The graphite clusters with more symmetry take a little less time. The diamond clusters composed of a single plane take less time than a bulk solid consisting of several sheets. The computation of clusters larger than these are not practical on a VAX 11/780.

III. SUMMARY AND FUTURE WORK

Clusters of carbons containing 40-50 atoms are potential models for diamond and graphite surfaces. The diamonds should be modeled as a bulk solid at least three sheets deep. Capped bonds potentially provide a good method for satisfying the valences on the edge of the cluster.

Current work is centered on obtaining the heats of formation of small molecules absorbed on these graphite clusters. These results should indicate the feasibility of using semi-empirical methods for estimating Van der Waals forces between lubricant sheets in a solid lubricant.

Any work beyond this point will depend critically on the availability of manpower and funding.

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